VOLATILITIES OF INORGANIC ELEMENTS IN COALS DURING ASHING

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INTRODUCTION

There are several reasons for requiring volatility information in coal:

a) Environmental
The flame temperature within the boiler furnace of a pulverized fuel power station may reach well above 1600°C when burning a bituminous coal. The higher the volatility of an element at temperatures of this magnitude then the higher will be the proportion of the element which will eventually escape to atmosphere, either in vapor form or in condensed form on unprecipitated fly ash particles. Elements which display some toxicity towards human, animal or plant life will therefore tend to impose a degree of detrimental impact on the environment.

b) Engineering design
The achievement of a satisfactory mass balance study of a coal combustion system must accommodate elements reporting to the primary bottom ash, precipitated and unprecipitated fly ash, and gaseous discharge components. Foreknowledge of volatility information can assist in the interpretation of data.

c) Analysis
Coal is a very complex heterogeneous matrix. Some techniques are suitable for the direct determination of many elements in whole coal samples while other techniques require an ashed sample.

d) Data base information
Many reports of elemental volatilities at various ranges of ashing temperatures and atmospheres have been published. An investigation covering a large number of elements, coal types, and ashing temperatures, would contribute significantly to an understanding of what could be expected under a given set of circumstances.

The literature on element volatility in coal is extensive. A summary has been compiled and discussed in the detailed NERDDP Report covering this work (1). When different reports are compared inconsistencies occur for many elements as ashing temperatures are raised from 370° to 2200°C. Several reports detailing ash derived from radiofrequency oxygen plasma ashing (RFA) at 150°C indicate quantitative retention of most elements studied making it a very suitable material for the analysis of inorganic elements in coal.

This investigation was designed to study the losses of 58 inorganic elements present at trace to minor concentrations in six coal samples.

EXPERIMENTAL

A set of six coals (four representative Australian bituminous coals and two US NBS standards, 1632A and 1635) were chosen to form the primary samples for this effort. Several other coals were selected to provide further information on specific elements.

Each of the coals was milled to less than 76 μm particle size in a slow speed Siebtechnik mill. The procedures for the preparation of the ash residues were as follows:

150°C(RFA) - multiple 0.6 g samples were processed in refractory boats with a layer loading of 1.5 mg/mm^2 in an LFE-504 Low Temperature Plasma Asher (150W power, 150 ml/min oxygen flow rate) until constant weight was achieved. The samples were removed from the asher three times daily and raked with a stainless steel spatula to present a fresh surface for oxidation. Total ashing time for each sample was approximately three days, except NBS1635 which required seven days.

370°C - samples were placed directly into a laboratory air oven maintained at the required temperature, and remained until constant weight was achieved (approx. 14 days).

815°C - samples were placed in a furnace at 200°C, and brought to 500°C over 30 min, transferred to a second muffle at 500°C and brought to 815°C over 30 min, then held at 815°C for 30 min.

1500°C - samples of 815°C ash were placed in a 10 ml platinum crucible (specially altered by the attachment of fine platinum wires to allow manipulation from above), lowered into the hot zone of a vertical tube furnace, and held at this temperature for 30 min. All of the residues from this procedure had fused, and were pulverized in a Siebtechnik mill.

The analytical methods employed for determining the 58 elements in this study were X-ray spectroscopy (XRF), instrumental neutron activation analysis (NAA), atomic absorption spectroscopy (AAS), inductively coupled plasma spectroscopy (ICP), specific ion electrode potentiometry (ISE), and optical emission spectroscopy (OES). The specific details for these procedures have been previously published (1-6). The elements determined by each technique are summarized in Table 1. In many cases, where possible, elements were determined by several methods.

RESULTS AND DISCUSSION

An element was considered volatile if the difference between its concentration in the starting coal and in the ash, on a normalized basis, was greater than the experimental uncertainty for a particular element. A greater than 20 percent change in concentration was usually required for the change to be considerd significant. The volatility of an element was designated inconclusive when it was very near the experimental uncertainty or if different analytical techniques indicated conflicting results.

The results of this study are summarized in Table 2. Only six of the 58 elements investigated undergo some degree of volatilization at temperatures up to 815°C. This group of elements--boron, bromine, cadmium, fluorine, mercury, and selenium--was augmented at higher temperature, 1500°C, by a further ten--arsenic, gallium, germanium, manganese, potassium, sodium, strontium, thallium, yttrium, and zinc--which were each volatilized from at least one of the coals. Note in Table 2 that Bi, Gd, Ho, and Te were below the limits of detection for all the six coals investigated, eliminating the evaluation of volatility trends. Other elements (In, Dy, and P) were below detection in four of the coals. Results for NBS1635 indicated seventeen elements were below limits of detection. Thus, under the oxidizing conditions prevalent during the preparation of the various coal ashes, there were 38 elements which at no stage were observed to undergo significant volatilization.

RFA Volatilization

Mercury was consistently retained in the RFA residue of each of the six coals studied in this project. Conversely, the literature has reported the consistent and unambiguous loss of mercury. Attention to details of RF ashing, which influence the actual temperature of the oxidation, possibly explains this discrepancy. For example, the sample layer loading within each sample container inside the RF ashing instrument, the particle size, the mineral matter content, and the chemical composition, could all play a part in influencing the localized temperature.

The implication of the literature was that bromine is volatilized. The 'difference' between the literature and the present work derives from there being a variable loss observed herein, with four coals showing definite volatilization, one (SC143B) showing retention, and one (NBS1635) being inconclusive.

Selenium is generally regarded as a relatively volatile trace element though consistently is retained under the conditions of RFA preparation. There was, however, the single incidence with SC146 in the present work for which this element was considered to have been volatilized.

Only fluorine was found to be volatilized significantly during the oxidation of each of the coals.

Low temperature ashing, although a time consuming procedure, is highly recommended for preparing coal samples for analyses where the analytical method to be used requires the carbonaceous material to be removed. Of all the elements surveyed in this study only a few (F, Br, B, and Se) indicated significant volatility. It is recommended that laboratories check their ashing procedures critically (especially for Hg) before attempting this approach however.

370°C Volatilization

At a temperature of 370°C selenium was significantly volatilized from four of the six coals. In contrast the literature implies that selenium is consistently lost under these ashing conditions.

Boron occupies a curious and special position, with regard to the volatility data in this work as well as to those literature reports which have addressed the lower temperature volatilization behavior of this element. Boron volatilization data implied that there were occasionally substantial losses at 370°C. However, the 815°C ash data for the above-mentioned coals indicated a retention of boron. The results of the present study may be interpreted in terms of respective kinetics for low temperature volatilization and higher temperature oxidative retention. Boron is well known to be predominantly associated with organic matter in coals, an affiliation which has been proposed to explain the high emissions of this otherwise refractory element in the stack gases from coal fired power stations (7). The competing reactions of organo-boron volatilization and oxidation must be considered to favor the former at low temperatures and the latter at higher temperatures. The absence of 370°C loss for all coals, plus the variable behavior with the NBS1635 ashes, implies a probable strong dependence of boron volatility upon the chemical forms of the element present in individual coals, and possibly localized oxidative conditions during the preparation of the ash residues.

815°C Volatilization

The 500°-900°C temperature range ashes have been the most extensively investigated in the literature, with 15 separate works being available for comparisons with the results of the present study. Fourteen elements listed as "inconclusive" retention from literature reports were found to be essentially retained in the 815°C ash in this study. This included Sb, As, B, Cr, Co, Cu, Ga, Pb, Mn, Mo, Sn, Ti, V and Zn. Cadmium was found to be volatilized in several coals at 815°C in contrast to literature reports where retention was claimed. All coals studied showed some significant loss of Se at this temperature. Sodium was found to be essentially retained in the six coals tested.

1500°C Volatilization

The very high temperature to which these ashes were heated yielded an increase in elemental volatilities from all coals. However, there was no element which was lost from every one of the six primary coals. Thallium was lost from five coals, arsenic from four, gallium and yttrium from two each, and germanium from one bituminous coal, with manganese, potassium, sodium, strontium, and zinc from NBS1635 only. In the literature, one report indicated consistent and complete volatilization of arsenic by 1400°C, while the alkalis, sodium and potassium, as well as strontium, were considered involatile. Cobalt and vanadium were not observed to have been volatilized from any of the coals of this study.

Environmental Considerations

The volatilities of the inorganic elements studied in this project are of considerable interest in relation to the classifications of potential environmental concern as assigned in a National Research Council Panel Report to trace elements in reference to impact on environmental quality and health (8). The exact reasoning behind one or other designation for a particular element is quite complex, taking into consideration such aspects as toxicity to human, animal and plant life, chemical reactivity following release into the environment, leachability by groundwaters, amongst others. These elements are categorized in Table 3 and listed also according to the following volatility designations as observed in this study:

<u>high</u> (volatilization generally observed in coals below 815°C)
<u>moderate</u> (volatilization observed for coals below 1500°C)
<u>low</u> (volatilization negligible at 1500°C)

Table 3 indicates that B, Cd, Hg, Se, and F are classified as moderate or greatest environmental concern and also high volatility. Both B and F have relatively large concentrations in most coals (>50 ppm), Se is generally $\sim$1 ppm or higher, and Hg and Cd tend to be lower than 1 ppm. This combination of toxicity, concentration, and volatility gives some qualitative emphasis to an elements possible environmental impact.

CONCLUSION

The investigation of the volatility behavior of 58 elements in coals, from analyses of the whole coals and their ashes prepared under static oxidizing conditions at temperatures up to 1500°C, showed that only very few elements are lost up to 815°C. This gives further support for utilization of low-temperature plasma ashing to prepare coal samples for analysis. By 1500°C, volatilization losses of nearly one-third of the inorganic elements studied became appreciable.

The most probable factors affecting the volatility of an element are the ambient chemical and physical states. Volatilization will depend upon the distribution of the element between various mineral phases or organically associated species in the coal, and upon the prevailing temperature and oxidizing or reducing conditions during combustion. Observations of boron and mercury volatilities under various conditions support this conclusion. Time effects may also be important, as completion of ashing under RFA and 370°C conditions takes many days. The present study could not, nor did it seek to, achieve a thorough assessment of these factors.

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Table 1. Methods Utilized for the Analyses of Coal and Coal Ash.

	NAA	XRF	OES	ICP	AAS	ISE		NAA	XRF	OES	ICP	AAS
Ag	X				X		Lu	X	X			
Al			X	X			Mg			X	X	
As	X	X					Mn	X	X	X	X	
B			X	X			Mo	X	X			
Ba	X	X	X	X			Na	X		X	X	X
Be			X				Ni	X	X	X	X	
Bi		X					P			X	X	
Br	X	X					Pb		X			
Ca			X	X			Rb	X	X	X		
Cd					X		Sb	X	X			
Ce	X	X					Sc	X	X			
Co	X	X	X				Se	X	X			
Cr	X		X	X			Si			X	X	
Cs	X	X					Sm	X				
Cu		X	X	X			Sn		X			
Dy	X	X					Sr		X	X	X	
Eu	X						Ta	X	X			
F						X	Tb	X				
Fe			X	X			Te		X			
Ga	X	X					Th	X	X			
Gd		X					Ti		X	X	X	
Ge		X					Tl		X			X
Hf	X	X					W	X				
Hg					X		U	X	X			
Ho		X					V		X	X	X	
In	X	X					Y		X			
K	X		X	X	X		Yb	X	X			
La	X						Zn	X	X	X	X	
Li				X			Zr		X	X	X	

Table 2. Elements with significant volatilization observed initially at indicated temperatures.

Coal Number (Rank Classification)	RFA, ∿150°C	370°C	815°C	1500°C
SC143B (Bituminous)	fluorine	bromine mercury	cadmium selenium	arsenic gallium thallium yttrium
SC146 (Bituminous)	bromine fluorine selenium	boron mercury	cadmium	-
SC147 (Bituminous)	bromine fluorine	boron mercury	selenium	arsenic cadmium thallium
SC151 (Bituminous)	bromine fluorine	boron mercury selenium	-	arsenic cadmium germanium thallium
NBS1632a (Bituminous)	bromine fluorine	boron mercury selenium	-	arsenic cadmium gallium thallium yttrium
NBS1635 (Subbituminous)	boron fluorine	mercury selenium	-	manganese potassium sodium strontium thallium zinc

Note 1. The following elements may be volatilized at 1500°C in the indicated coals, however the data is either not sufficiently accurate for a firm conclusion to be drawn or there is unresolved conflict between data from different analysis techniques:

Ce (NBS1635)	Pb (SC147)
Ga (SC146)	K (NBS1632

Note 2. Boron was lost only at 370°C from SC146, SC147, SC151 and NBS1632a, but from the RFA, 370°C and 1500°C residues from NBS1635. No B was lost from any 815°C ash preparation.

Note 3. Those elements which were below the limits of detection are summarized as follows:

All coals	Bi, Gd, Ho, Te	NBS1632A	Dy, In
SC143B	Dy, In, P	NBS1635	As, Br, Cd, Cs, Co, Dy
SC146	In		Ge, Hf, In, Lu, Rb, Sb,
SC147	In, P		Sb, Sn, Ta, Th, U, Yb

Table 3. Volatility classifications of 'elements of concern'

NRC PECH Panel Classification (8)	element	volatility
greatest concern	arsenic	moderate
	boron	high
	cadmium	high
	lead	low
	mercury	high
	molybdenum	low
	selenium	high
moderate concern	chromium	low
	copper	low
	fluorine	high
	nickel	low
	vanadium	low
	zinc	moderate
minor concern	antimony	low
	barium	low
	bromine	high
	chlorine	-
	cobalt	low
	germanium	moderate
	lithium	low
	manganese	moderate
	sodium	moderate
	strontium	moderate
radioactive	thorium	low
	uranium	low
elements of concern but with negligible concentrations	beryllium	low
	tellurium	-
	thallium	moderate
	tin	low

Refer to text for volatility classification bases.